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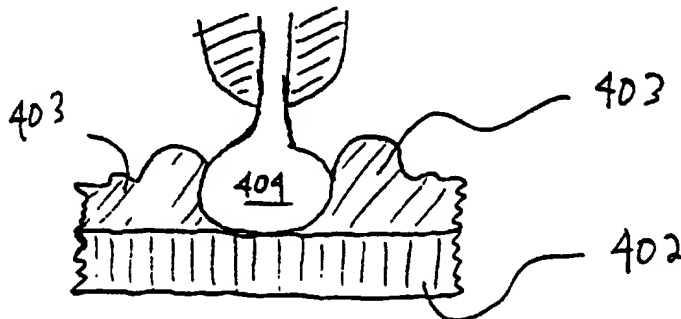
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(54) Title: METHOD AND APPARATUS FOR ENABLING CONVENTIONAL WIRE BONDING TO COPPER-BASED BOND
PAD FEATURES



(57) Abstract: A method is described comprising removing an oxide from a surface and then commencing application of a passivation layer to the surface within 5 seconds of the oxide removal. The surface may be a copper surface which may further comprise a bonding pad surface. Removing the oxide may further comprise applying a solution comprising citric acid or hydrochloric acid. Applying the passivation layer may further comprise applying a solution comprising a member of the azole family where the azole family member may further comprise BTA. The method may also further

comprise completely applying the passivation layer 35 seconds after commencing its application.

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 10277 A (ELECTROCHEMICALS INC) 27 May 1993 (1993-05-27) page 7, line 10 -page 10, line 8 ---	1-7
X	DATABASE WPI Section Ch, Week 197808 Derwent Publications Ltd., London, GB; Class E19, AN 1978-14699A XP002143960 & JP 53 001654 A (FURUKAWA ELECTRIC CO LTD), 9 January 1978 (1978-01-09) abstract --- -/--	1,2,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter national Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YIQI FENG ET AL: "Corrosion protection of copper by a self-assembled monolayer of alkanethiol" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, JAN. 1997, ELECTROCHEM. SOC, USA, vol. 144, no. 1, pages 55-64, XP002143958 ISSN: 0013-4651 page 56, column 2, line 3 - line 19 figure 1	1,2,5
X	ANONYMOUS: "Protection of M1 Cu Surface Prior to M2 Evaporation. November 1981." IBM TECHNICAL DISCLOSURE BULLETIN, vol. 24, no. 6, 1 November 1981 (1981-11-01), page 2989 XP002143959 New York, US the whole document	1-3
X A	US 5 858 109 A (HYMES DIANE J ET AL) 12 January 1999 (1999-01-12) column 3, line 17 - line 24 column 4, line 65 -column 5, line 40 figure 1	9,13,30, 33 17,19-22
X A	US 5 868 863 A (HYMES DIANE J ET AL) 9 February 1999 (1999-02-09) cited in the application column 1, line 29 - line 34 column 2, line 57 - line 46 column 5, line 4 - line 37 column 6, line 38 - line 54	9,10,30, 33 17,19, 20,26
X A	EP 0 878 831 A (TOKYO SHIBAURA ELECTRIC CO) 18 November 1998 (1998-11-18) column 2, line 33 - line 41 column 3, line 40 - line 58 column 5, line 31 - line 35 column 9, line 30 - line 31	9,13,30, 33 17,20,22
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/05787

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 709 755 A (KUO SO WEIN ET AL) 20 January 1998 (1998-01-20) the whole document ---	17-33
A	DE 44 44 388 A (ATOTECH DEUTSCHLAND GMBH) 30 May 1996 (1996-05-30) page 3, line 25 - line 58 ---	34-37
A	DATABASE WPI Section EI, Week 199531 Derwent Publications Ltd., London, GB; Class U11, AN 1995-238055 XP002150984 & JP 07 147300 A (HITACHI LTD), 6 June 1995 (1995-06-06) abstract -----	34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/05787

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims: it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8

Method to remove an oxide form a surface and to apply subsequently a passivation layer.

The prior art (W09310277) describes the reduction of the oxidized surface of a copper layer and the passivation of the reduced surface with a passivating solution (e.g. BTA).

The new feature in claim 8 is the process time of 35 seconds, required to completely apply the passivation layer.

The special technical feature as defined in rule 13(2) PCT, is the process time of 35 seconds, required to completely apply the passivation layer.

The objective problem is to rapidly form a layer that prevents copper oxidation.

2. Claims: 9-33

Method and apparatus using a brush to apply liquids to a wafer surface.

The prior art (W09310277) describes the reduction of the oxidized surface of a copper layer and the passivation of the reduced surface with a passivating solution (e.g. BTA).

The new features in claims 9-33 are the method and the apparatus to remove and/or to form a layer on a semiconductor wafer by applying a liquid on the wafer surface using a brush.

The special technical features as defined in rule 13(2) PCT, are the method and the apparatus to form a layer on a semiconductor wafer, by applying a liquid on the wafer surface using a brush.

The objective problem is to have a cost effective way of applying a liquid to a wafer surface.

3. Claims: 34-37

Method for forming a wire bond to a wafer.

The prior art (W09310277) describes how to reduce the oxidized surface of a copper layer and how to passivate the reduced surface with a passivating solution (e.g. BTA).

The new feature in claims 34-37 is the application of a bond

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

to a wafer surface by punching through the passivation layer.

The special technical feature as defined in rule 13(2) PCT, is the application of a bond to a wafer surface by punching through the passivation layer.

The objective problem is to obtain a good ohmic contact between the bonding pad and the bonding wire.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter: International Application No

PCT/US 00/05787

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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(60) Parent Application or Grant LAM RESEARCH CORPORATION [/]; O. LL Hugh [/]; O. HYMES, Diane, J. [/]; O. PENILLA, Albert, S. ; O.		
(54) Title: METHOD AND APPARATUS FOR ENABLING CONVENTIONAL WIRE BONDING TO COPPER-BASED BOND PAD FEATURES		
(54) Titre: PROCEDE ET APPAREIL PERMETTANT UNE CONNEXION DE FILS CLASSIQUES A DES DISPOSITIFS A PLACES DE CONNEXION DE CUIVRE		
(57) Abstract		
<p>A method is described comprising removing an oxide from a surface and then commencing application of a passivation layer to the surface within 5 seconds of the oxide removal. The surface may be a copper surface which may further comprise a bonding pad surface. Removing the oxide may further comprise applying a solution comprising citric acid or hydrochloric acid. Applying the passivation layer may further comprise applying a solution comprising a member of the azole family where the azole family member may further comprise BTA. The method may also further comprise completely applying the passivation layer 35 seconds after commencing its application.</p>		
(57) Abrégé		
<p>L'invention concerne un procédé qui comporte les étapes consistant à : éliminer un oxyde d'une surface et commencer ensuite à appliquer sur celle-ci une couche de passivation dans les cinq secondes suivant l'élimination de l'oxyde. La surface peut être une surface de cuivre pouvant comporter en outre une surface de plage de connexion. L'élimination de l'oxyde peut en outre comporter une étape d'application d'une solution contenant de l'acide citrique ou de l'acide chlorhydrique. L'application de la couche de passivation peut également comporter une étape d'application d'une solution contenant un élément de la famille des azoles, cet élément pouvant comprendre en outre du BTA. Le procédé peut aussi comporter l'étape consistant à appliquer entièrement la couche de passivation en 35 secondes, à partir du début de l'application.</p>		

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(30) Priority Data: 09/282,596 31 March 1999 (31.03.99) US			
(71) Applicant: LAM RESEARCH CORPORATION [US/US]; 4650 Cushing Parkway, Fremont, CA 94538-6516 (US).			
(72) Inventors: LI, Hugh; 1901 Halford Avenue, Apt. 9, Santa Clara, CA 95051 (US). HYMES, Diane, J.; 5617 Algowquin Way, San Jose, CA 95138 (US).			
(74) Agent: PENILLA, Albert, S.; Martine Penilla & Kim, LLP, 710 Lakeway Drive, Suite 170, Sunnyvale, CA 94086 (US).			Published Without international search report and to be republished upon receipt of that report.
(54) Title: METHOD AND APPARATUS FOR ENABLING CONVENTIONAL WIRE BONDING TO COPPER-BASED BOND PAD FEATURES			
(57) Abstract			
<p>A method is described comprising removing an oxide from a surface and then commencing application of a passivation layer to the surface within 5 seconds of the oxide removal. The surface may be a copper surface which may further comprise a bonding pad surface. Removing the oxide may further comprise applying a solution comprising citric acid or hydrochloric acid. Applying the passivation layer may further comprise applying a solution comprising a member of the azole family where the azole family member may further comprise BTA. The method may also further comprise completely applying the passivation layer 35 seconds after commencing its application.</p>			

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METHOD AND APPARATUS FOR ENABLING CONVENTIONAL WIRE
BONDING TO COPPER-BASED BOND PAD FEATURES

FIELD OF INVENTION

The field of invention relates to thin film processing and, more specifically, to the field of processing techniques for semiconductor integrated circuits employing copper based metallization technology.

BACKGROUND OF THE INVENTION

In the manufacture of advanced semiconductor devices, copper (Cu) is beginning to replace aluminum (Al) as the material for metallization. Cu has become desirable due to its lower resistivity and significantly improved electromigration lifetime, when compared to Al.

A problem with Cu based metallurgy, however, involves the rate at which native oxides form on exposed regions of copper. In a free air ambient, it is reported that copper oxides grow 20 Angstroms (\AA) within the first minute; while within water environments copper oxides grow 50\AA within the first minute. Frequently these native oxides are undesirable. That is, as the copper region is typically used to electrically interconnect various devices within an electrical circuit, the formation of the oxide represents an undesirable reduction of conductance. Thus, cleaning, ambient control and/or processing approaches unique to copper metallurgy based manufacturing processes are typically used to control mitigate, or at least limit, the effects of the oxide growth.

5 One particular problem area concerns bonding pads used for
input/output (I/O) connections from the semiconductor chip to its associated
10 package. Specifically, copper based metallization technologies having copper
bonding pads experience bond quality problems which are caused by the growth
15 of a relatively thick native oxide on the copper bond pad.

Typically, a wire is bonded as shown in Figure 1. Referring to Figure 1a, a
capillary 101a threaded with a (typically Gold (Au) or Al) wire 104a having a ball
20 102a formed at the capillary tip 105a is centered over a chip's bond pad 103a and
(referring now to Figure 1b) pressed against the face of the bond pad 103b. Then,
10 typically, either thermosonic or thermocompressive energy is applied at the
25 capillary tip 105b to adhere the ball 102b to the bond pad 103b. As shown in
Figures 1c and 1d, after the ball 102c is adhered to the bond pad 103c, the
30 capillary 101c moves to a package lead 106 where the wire 104d is subsequently
wedge bonded to the package lead 106.

15 Unfortunately, in standard manufacturing processes, a native oxide (not
35 shown in Figure 1a) forms over the copper bond pad 103a before the ball 102a
makes contact with the pad 103a. The native oxide prevents a bond from
40 forming between the wire and the underlying copper pad. Good bonds typically
exhibit an intermetallic layer between the ball 102 and the bond pad 103.

20 As discussed, the native oxide is formed prior to the application of the ball
45 102 to the bond pad 103. Standard manufacturing processes typically form the
bond pad structure immediately following the last (or highest) metallization
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5 layer of the interconnect structure of the semiconductor wafer. After the last
metallization layer is formed, the metal layer is polished (e.g., by a Chemical
10 Mechanical Polish (CMP)) to a specified thickness range.

After polishing, the semiconductor wafer is cleaned to remove unwanted
5 particulates from the surface of the wafer, most of which result from the prior
15 polishing steps. Native bond pad oxides formed after polishing and before
cleaning may be removed by the cleaning process depending on the cleaning
20 chemistry used. After cleaning, the semiconductor wafers are dried, tested and
diced. Each individual die is then placed in a chip carrier and epoxied at
10 elevated temperature to a die package before the wire bonding procedure
25 commences.

The entire "post cleaning" process described above results in copper bond
30 pad exposure to an oxygen based ambient/environment at room temperature as
well as in an a thermal curing oven for substantial periods of time. As a result, it
15 is difficult to prevent native oxide growth on the exposed bond pads without
35 introducing costly complications to the standard manufacturing sequence just
described (for example, one approach is to plasma etch and then deposit a
40 relatively thick layer of another metal film, such as Ni; this would then be
followed by a second deposition of palladium and/or gold).

20 Thus, a cost effective way of controlling the native oxide growth on the
45 copper bond pads is needed.

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SUMMARY OF THE INVENTION

A method and apparatus are described for removing an oxide from a surface and then commencing application of a passivation layer to the surface within 5 seconds of the oxide removal. The surface may be a copper surface which may further comprise a bonding pad surface. Removing the oxide may further comprise applying a solution comprising citric acid or hydrochloric acid. Applying the passivation layer may further comprise applying a solution comprising a member of the azole family where the azole family member may further comprise BTA. The method may also further comprise completely applying the passivation layer 35 seconds after commencing its application.

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BRIEF DESCRIPTION OF THE DRAWINGS

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The present invention is illustrated by way of example and not limitation in the figures of the accompanying drawings, in which like references indicate similar elements, and in which:

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5 Figures 1A thru 1D show a typical wire bonding process.

Figure 2 shows an example of a brush scrubbing system.

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Figure 3 shows an example of a brush used within the brush scrubbing system of Figure 2.

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Figures 4A thru 4E show a method for forming a wire bond to a copper surface.

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DETAILED DESCRIPTION

Methods and apparatuses are described for processing wafers. In the following description, numerous details are set forth, such as distances between components, types of molding, etc. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without these specific details. In other instances, well-known structures and devices are shown in block diagram form, rather than in detail, in order to avoid obscuring the present invention.

In one embodiment, the manufacturability and/or cost-of-ownership of copper based metallization technology are improved with the processing techniques described herein. As copper suffers from continuous oxide formation, methods and apparatuses described herein control the detrimental effects caused by the oxide growth.

In one embodiment, the processing of wafers includes removing an oxide from a surface and then commencing application of a passivation layer to the surface (e.g., a copper surface, a bonding pad surface, etc.). The oxide may be removed by applying a solution of either citric acid or hydrochloric acid to the surface. The passivation layer may be applied by applying a solution to the surface, where the solution is a member of the azole family (e.g., BTA, etc.). In one embodiment, the passivation layer is applied within 5 seconds of the oxide removal and is completed approximately 35 seconds after commencing its application.

5 In one embodiment, the application of the passivation layer is performed by the use of a brush and a liquid (e.g., a wet chemistry) supplied to a brush.

10 Such a technique is equally applicable to the application of other layers as well.

In one embodiment, the liquid reacts with the wafer surface to form the layer. In

15 5 one embodiment, the brush may be part of a wafer processing system that is typically designed for brush scrubbing and the liquid is provided to the core of the brush for chemical delivery through the brush. Note that chemical delivery through the brush is not required and the liquid may be dripped, for example, onto the brush for application thereby.

25 10 These and other embodiments of the present invention may be realized in accordance with the following teachings and it should be evident that various modifications and changes may be made in the following teachings without departing from the broader spirit and scope of the invention. The specification and drawings are, accordingly, to be regarded in an illustrative rather than
30 15 restrictive sense and the invention is measured only in terms of the claims.

35 For example, although the discussion below is directed mostly to copper based process technologies for semiconductor IC bond pads, it will be evident to those skilled in the art that the broader scope of the teachings herein may be
40 applied to other technologies employing materials susceptible to aggressive and/or unwanted oxide formation. For example, magnetic recording or
45 20 magneto optical based processes similarly involve transition metals (such as Iron, Cobolt and Nickel) or their alloys which may suffer from unwanted oxide film

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5 growth. Furthermore, the teachings herein may also be employed to
semiconductor based processes using other materials (besides copper) that
10 similarly suffer from aggressive or unwanted oxide growth. Further still, the
teachings herein may also be applied to other packaging technologies (besides
5 wire bonds), for example: flip chip technologies as well as ball grid arrays and
15 pin grid arrays.

The bond pads are typically formed after the final layer of interconnect
20 metallization is formed. Therefore, minimal amount of disruption is added to
the manufacturing process by employing a brush scrubber after the post CMP
10 wafer cleaning step to remove the oxide and deposit the passivation layer. A
25 minimal amount of disruption to the overall manufacturing process may also
result if the oxide removal and passivation layer application methods are
30 performed either after the wafer is tested or just prior to wire bonding.

A brief explanation of a typical method used to clean a wafer with a brush
15 scrubber is now described. Figure 2 shows an exemplary brush scrubber (also
35 referred to as a system). The scrubber includes a number of stations. Each of
these stations typically represents one or more steps in the wafer cleaning
40 process. Contaminated wafers (or substrates) are loaded at one end of the
system and cleaned and dried substrates are unloaded from the other end of the
20 system. That is, contaminated substrates are loaded into a wafer cassette 280 and
45 the cassette 280 is then placed into the wet send index station 210. After cassette
280 is placed into the wet send indexer station 210 the substrates are
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5 automatically removed from the cassette 280 and placed, one at a time, into the outside brush station 220.

10 In the outside brush station 220, a substrate is processed through a first scrub. Typically, the substrate is treated with a solution (such as ammonium
5 hydroxide (NH_4OH), HF or SC1) during the first scrub. The solution is applied
15 to the substrate through the brushes 221. The substrate itself may rotate underneath brushes 221 to help apply the solution. Wafers usually traverse the
20 brush stations 220, 230 via hardware that transport the wafer from one end of the brush station to the other.

10 The scrubbed substrate is then automatically removed from the outside
25 brush station 220 and placed into the inside brush station 230. Most scrubbers are capable of transporting the wafer from the first to second station in 5 seconds
30 or less. In the inside brush station 230, the substrate is processed through a second scrub. Again, the wafer is treated with another solution (for example,
15 diluted hydrofluoric acid (HF)) during the second scrub. As in the first scrub
35 step, the solution is applied to the substrate through brushes 231. After the second scrub the substrate is then automatically removed from the inside brush
40 station 230 and placed into the rinse, spin and dry station 240. The substrate is then transported to the output station 250 and then placed into cassette 281.

20 An exemplary brushing apparatus 300 used for scrubbing wafers as well
45 as applying various solutions is shown in Figure 3. A solution is typically a mixture of more than one liquid (such as deionized (DI) water and an acid). The
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5 embodiment of Figure 3 may supply liquids through supply lines 310 and 320. Various liquids may be applied sequentially, that is, one at a time; or in the
10 alternative, at the same time. Supply lines 310 and 320 run into delivery tube 370. Delivery tube 370 delivers the solution into the hollow core 330 of the brush
15 340 at a predetermined flow rate. The supply lines 310 and 320 are therefore in fluid communication with the brush core 330. Usually, as brush 340 is being saturated with solution it is rotated by rotation device 360. Rotation device 360
20 turns brush 340 in a clockwise (or counterclockwise) manner, which applies the solution to the substrate through slots or holes 350. Because brush 340 is wet
25 with solution, the solution which is brought in contact with the wafer is applied to the substrate. More details on brush scrubbing technology may be obtained from U.S. Patent No. 5,868,863 entitled Method and Apparatus for Cleaning of
30 Semiconductor Substrates Using Hydrofluoric Acid (HF).

Furthermore, other brush scrubbing equipment, rather than injecting
15 liquid into the core of a brush, applies fluid over the brush or wafer. Therefore, such equipment also employs a wet brush which relatively uniformly applies
35 solution to the wafer. Regardless of which type of equipment is employed (either a system that flows liquid through a brush or a system that applies liquid
40 over a brush or wafer), both may be referred to as equipment that applies liquid with a brush, since the brush is wet with liquid in both systems.
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45 The discussion below describes various methods and apparatus that may be employed to address one or more problems, such as the oxide formation

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5 problems, that occur on copper bonding pads for semiconductor ICs. Generally,
referring to Figure 4, the native oxide 401 is first removed from the bond pad 402
10 (as shown in Figures 4a and 4b) and then a passivation layer 403 is immediately
(i.e., commenced within 5 seconds or less) formed over the bond pad 402 (as
5 shown in Figure 4c). Since the passivation layer covers the bond pad, it prevents
15 native oxide formation during transport and downstream processing (such as
testing, dicing, thermal annealing etc.). Furthermore, the passivation layer is
20 designed such that the wire bond 404, when its bonded, may be bonded through
the passivation layer to the copper pad (as shown in Figures 4d and 4e). As such,
10 the passivation layer also does not significantly interfere with the integrity of the
25 bond formed between the wire bond and the copper bonding pad. The
passivation layer is therefore a barrier to native oxide formation, while
30 permitting the wire bonding.

In order to prevent native oxide formation on the bonding pad, the
15 passivation layer has enough thickness and density to adequately prevent the
35 interaction of oxygen ambients with the surface of the copper pad. Furthermore,
in order to be transparent to the wire bonding process, the passivation layer is
40 not too thick (such that its presence significantly interferes with the wire bonding
to the extent that the bond's integrity falls beneath acceptable standards). Thus
20 the thickness and density have a first bound determined by oxide growth
45 dynamics and a second bound determined by wire bonding dynamics.

5 Furthermore, passivation layers are different from adhesion and/or
barrier layers. A form of adhesion layer is the aforementioned metal film (such
10 as Ni/Au or Ni/Pd) deposited over the copper pad before the wire bond.
Adhesion layers are a transition layer between the copper bond pad and the wire
5 bond itself. That is, the wire bond and the copper pad each adhere only to the
15 transition layer which ultimately promotes overall mechanical connection of the
wire bond to the die. However, since the adhesion layer is deliberately used to
20 prevent direct contact between the copper pad and the wire bond, it must be
conductive. With adhesion layers, electrical current does not flow directly
10 to/from the bond pad from/to the wire bond without traversing the adhesion
25 layer.

By contrast, the passivation layer discussed herein is designed to be
30 punched through by the wire bonding process. As such there is some direct
contact between the wire bond and the conducting pad. Thus, with passivation
15 layers, current may or may not flow through the passivation layer since at least
35 some current flows directly to/from the bond pad from/to the wire bond.

As discussed, after the final metallization and its associated polish, the
40 wafer is typically further subjected to cleaning, drying, testing, dicing and
thermal annealing. After the individual chips are diced, each one is typically
20 placed in a chip carrier and then epoxied to its package prior to wire bonding.
45 The native oxide may be removed and the passivation layer applied anywhere
within the aforementioned process. For example, after testing, the wafer may be
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5 subjected to an oxide removal step followed by a passivation layer application step.

10 As discussed, native oxides form rapidly on copper that is exposed to environments that comprise oxygen (such as air or water). Thus, in such an
5 environment, once the native oxide is removed, the passivation layer should be
15 applied as soon as practicable in order to reduce native oxide regrowth. Alternatively, the native oxide may be removed in an oxygen free and/or
20 reducing environment. Lacking ambient oxygens, native oxides may not grow, allowing for greater delay between the removal of the native oxide and the
10 application of the passivation layer (provided the environment remains oxygen
25 free for the duration of the delay).

As discussed ahead, the removal of the oxide step as well as the
30 application of the passivation layer may be performed in any of a number of ways known in the art (such as baths, sprays etc.). However, one embodiment
15 involves use of a brush scrubber (described in reference to Figures 2 and 3) as the
35 apparatus for both removing the oxide and applying the passivation layer.

The discussion above concerning the operation of the scrubber system
40 suggests at least seven process parameters may be involved in the application of solutions through scrubbing brushes: 1) the rotational speed of the brush (i.e.,
20 brush speed); 2) the shear force of the brush (i.e., brush force) which typically
45 correlates with the height of the brush over the wafer and the type/shape of bristles on the brush; 3) the speed of the rollers (i.e., roller speed) used to rotate
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5 the wafer beneath the brush(es); 4) the length of time a wafer spends in a station
(i.e., process time); 5) the flow rates of the liquids applied to the brushes (i.e.,
10 flow rate); 6) the solution composition as well as the various concentrations of
the specific solutions applied and finally, 7) the temperature.

15 5 Generally, for any system, the roller speed and wafer process time
determine the number of rotations a wafer makes beneath the brush. The roller
speeds and wafer process times described herein were performed on 200 mm
20 diameter wafers in a system having 40 mm diameter rollers.

The following discussion addresses these parameters settings for both the
10 removal of a copper native oxide as well as the application of a passivation layer.
25 As discussed, brush scrubbing systems are traditionally used for cleaning wafers.
This involves the removal of contaminants in the form of discrete particulate
30 and/or film-like residue as well as the cleaning solution itself (during the rinse,
spin and dry stage). The following described method, however, involves the
15 unique application of brush scrubbing technology to the intentional deposition of
35 a thin film layer (e.g., the passivation layer) to a wafer surface. Furthermore, the
discussion herein is also unique in that it teaches the formation of an ultra thin
40 layer (such as 20Å or less). As discussed ahead, however, processes may be
varied to obtain layers of thickness above or below 20Å. Even further, ultra thin
20 layers are created with a wet chemistry process (i.e., the application of liquids to
45 a wafer process). Typically, wet chemistry processes (such as sprays or baths)
produces film thicknesses on the order of microns. Thus, the use of a brush

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5 within a brush scrubbing system as a device to apply a layer of material involves
a number of unique contributions. Consistent with this, the apparatus of Figure
10 2 may now also be viewed simply as a brushing system as opposed to only a
brush scrubbing system.

15 In most cases wafers require cleaning (with brush scrubbers as discussed
above) after CMP. The oxide removal and passivation layer application steps
may be applied immediately after this wafer cleaning step. In such an instance,
20 the wafers may be reinserted into the wafer input cassette 280 (referring briefly
back to Figure 2) immediately after they are removed from the output cassette
10 281 (the system having just performed the post CMP wafer cleaning). Also,
25 industry trends are currently integrating CMP polishers with brush cleaning
systems. Integrated systems may or may not prohibit reuse of the wafer brush
cleaning apparatus (depending on accessibility of the brushing station input
30 cassette). If an integrated system prohibits individual brush scrubbing use, a
15 separate stand-alone brush scrubber may be employed to implement the method
35 described ahead. In alternate embodiments, as previously suggested, the oxide
removal and passivation layer application may also be inserted at other
40 manufacturing stages, besides just after CMP, such as just after wafer testing or
just prior to wire bonding or in a rework cycle which includes these process
20 steps. Furthermore, in other possible alternative embodiments, it may be
45 necessary to passivate copper metallization beneath the highest metal level (such

5 as the first or second metal layers). The invention herein may also be used for such an application.

10 The native oxide must be removed before the passivation layer is applied. The native oxide may be removed by a number of different solution chemistries.

15 5 Usually, an acid or other solution is diluted in DI water. For example citric acid having a 0.2% concentration in DI water and a pH level of 2.0, hydrochloric acid (HCl) having a 0.1% concentration in DI water, malic acid having a 0.2% concentration in DI water or malonic acid having a 0.2% concentration in DI water may all be used where all concentration levels are by weight.

20 10 Furthermore, each of these concentration levels may be varied depending on, for example, the thickness of the oxide to be removed or the desired processing time. Thus ranges at least as wide as .005% to 0.5% for citric, malic and malonic acids and 0.01% to 0.2% for HCl may also be used. Furthermore, any of the above described solutions may be further buffered by (i.e., also add) 100 ppm to 0.2% of 30 15 ammonium hydroxide. Other solutions known in the art for removing oxides may also be applied.

35 40 The process time and solution flow rates may be typical values currently employed during standard wafer cleaning processes (such as a process time of 35 seconds and a solution flow rate of 500cc/min). The general idea is that the 45 20 wafer should be subjected to enough solution for enough time to substantially remove the oxide without causing damaging over etching effects to the material(s) residing beneath the oxide and to other features on the wafer. This 50

5 guideline also extends to the above described acidic concentration levels. That is,
higher acid concentration solutions should correspond to less process time
10 and/or flow rates as compared to lower acid concentration solutions. Also
consistent with this guideline, the employed brush speeds, roller speeds and
5 forces may be typical of those used for oxide water cleaning such as 120 rpm, 40
15 rpm and 2.5 lbs respectively. Again, various ranges for these parameters are
suitable provided the brushing is not too passive (resulting in under etched
20 oxide) or too aggressive (resulting in wafer or feature damage). The temperature
may be anywhere from room temperature to 50°C. Oxide removal dependence
10 on temperature is generally: the higher the temperature, the greater the rate of
25 removal.

After the oxide is removed the passivation layer is applied. Before
30 discussing the specific processing parameters used within the brushing station to
apply the layer, however, a brief discussion concerning the dynamics of the
15 transport of the wafer will be helpful. As discussed, native oxides on copper
35 have very aggressive growth rates. Essentially, in an environment having
oxygen (such as the free air ambient within a brushing station), oxides begin to
40 grow immediately after they are cleaned. As such, it is desirable to minimize the
time between the removal of the oxide and the application of the passivating
20 layer. As discussed, most scrubbing equipment is capable of transporting the
45 wafer from the first to second station in 5 seconds or less. Generally, the quickest
transport time achievable should be employed. As a rule of thumb, the transport
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5 time should consume 5 seconds or less. However, as discussed ahead, this time period may be extended depending on the amount of etchant left on the surface.

10 In a scrubbing system, the wafer moves horizontally from the first (i.e., oxide removal) brushing station 220 to the second (i.e., passivation layer application) brushing station 230 (referring briefly back to Figure 2) on hardware
15 beneath the wafer. That is, the wafer surface is perpendicular to the direction of gravity as it moves from the first 220 to second 230 station. Also, since the wafer
20 is typically "rightside up" (meaning the devices and metallization are facing the upper brush(es) of the scrubber), and since the brush(es) are removed from the
25 wafer surface before the wafer is transported to the second station; a coating of oxide removal solution (i.e., the solution employed in the first brush station) remains on the wafer surface as it moves from the first to second brushing
30 station. This has a beneficial effect as discussed below.

If the brushes remained on the wafer surface as the wafer left the station
15 the oxide removal solution would be wiped off of the wafer, especially if the solution flowing from the brushes ceased. If the solution were wiped off the
35 surface, the copper bond pads would be exposed to free air resulting in immediate undesired oxide growth. However, since particular scrubbing
40 systems (such as the Synergy™ brush scrubber from Ontrak Systems) simply lift the brushes in the first brushing station just before the wafer begins to exit, the
45 wafer is not wiped clean, resulting in a protective "puddle" of oxide etching

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5 solution over the wafer surface which deters oxide formation during the wafer transport between the scrubbing stations.

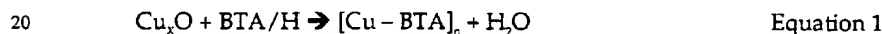
10 Thus leaving the oxide removal solution over the wafer surface is desirable as it provides some margin for the time between oxide removal and
5 passivation layer application. Nevertheless, given the rate of copper oxide
15 growth, the passivation layer should be applied as soon as possible or practicable once the oxide is removed. Generally, the passivation layer should be applied
20 within 5 seconds of the oxide removal step. Thus, equipment settings should be set to transport the wafer between stations but the puddle of etchant should
10 provide some margin beyond this time.

25 As an alternate approach, the oxide removal solution as well as the passivation layer solution may be both applied within the first scrubbing station.
30 That is, the oxide removal solution is first applied with a first station brush followed by a flow of the passivation layer solution with the same first station
15 brush. This approach simplifies the procedure as the wafer does not require
35 passage to a second station. Furthermore, the timing between application of the removal solution and application of the passivation layer solution is no longer
40 limited by the hardware responsible for transporting the wafer from the first to second scrubbing station.

20 Continuing with the "two-station" approach as an example, once the
45 wafer enters the second station a solution is immediately applied (through the brushes) that converts to a solid, stable passivation layer after exposure to the
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5 copper bond pad surface. The layer may also be referred to as a film. The
solution chemistry is generally comprised of members of the azole family.
10 Azoles, such as Benzotriazole (BTA), are known to provide protection against the
growth of native oxides on copper. BTA is currently the most widely-used
5 passivating agent for Copper and is the major component of many commercially
available solutions used for copper oxide prevention (such as StopOx™ from
Applied Chemical Technologies, Inc.). Other azoles that have been used for
20 copper oxide prevention include Indazole, Benzimidazole, Indole and Methyl
Benzotriazole. Furthermore, since PC board (PCB) technology employs copper
10 interconnects, passivation chemistries based on triazole and imidazole (used in
the Organic Solderability Preservatives (OSPs) used for PCB processes) may also
25 be used.

30 BTA and other azoles form a protective layer according to a chemical
reaction. Before the chemical reaction, pure BTA (or a diluted solution of BTA) is
15 in a liquid state. However, upon exposure to copper, a chemical reaction causing
35 a solid passivating film on the copper results. Particulates are any matter in a
solid phase (which includes polymers). These particulates form the passivation
40 layer. For BTA the chemical reaction is usually expressed as:



5 where $[\text{Cu-BTA}]_s$ is the solid film material and Cu_xO is believed to result
from the reaction of Cu with dissolved O_2 .

10 As discussed, the thickness of the passivation layer may have a minimum
bound necessary to substantially prevent further oxide growth and an upper
15 bound necessary to remain transparent to the bonding process. The specific
bonding parameters (such as frequency or time) needed to form acceptable
bonds may vary depending on the bond tool manufacturer as well as the
20 passivation layer thickness and its associated uniformity. Generally, more
bonding energy may be needed as passivation layer thickness (or thickness
variation) increases. As various bonding tools may be able to apply more or less
25 energy (and/or vary other parameters) the upper bound of the passivation layer
thickness may depend on the specific bonding tool employed.

30 As for the minimum bound, BTA passivation layer success is related to
another important film characteristic (besides thickness): density. Thick layers of
15 highly porous BTA would be an unacceptable passivation layer since the oxygen
would make contact to the copper pad through the pores in the BTA film. Thus
35 thin films of dense (i.e. low porosity) BTA are desirable. Film porosity is related
to the coating techniques applied (such as the type of brush used, the brush
40 speed, flow rates etc.). Generally, techniques that promote BTA coverage over
the entirety of the wafer surface, rather than spotty or blotchy coverage, diminish
45 porosity.

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Consistent with this, BTA film density is related to the concentration level of BTA in the solution. Generally, higher concentrations of BTA tend to provide better BTA coverage over the wafer surface resulting in denser films. Higher BTA concentrations also yield thicker films since more BTA is available for the reaction expressed in Equation 1. Thus, higher levels of BTA concentration yield dense films (desirable) with greater thickness (undesirable).

In order to take advantage of the benefits of higher BTA concentrations (i.e., more dense films) while simultaneously reducing, or even minimizing, the potential detriments of higher BTA concentrations (i.e., thick films), BTA coating uniformity should be controlled. Thus not only should the application techniques promote BTA coverage (i.e., ensure at least a minimum amount of BTA is exposed over the entire wafer surface), the techniques employed should also promote uniformity of the coverage (i.e., minimize the variation in the amount of BTA coverage over the entire wafer surface).

Uniform coatings of concentrated BTA over the entire wafer surface help keep thickness down while ensuring dense films as discussed below. Films not exhibiting good uniformity tend to require higher concentrations of BTA in order to maintain acceptable density levels. Non uniform BTA coverage of highly concentrated solutions results in some wafer regions exposed to high amounts of BTA (resulting in thick film regions) and other wafer regions exposed to moderate amounts of BTA (resulting in less thick film regions). Thus the film is characterized as having uneven thickness across the wafer. In such a case, since

5 the BTA concentration was high, both the thick regions and less thick regions
have sufficient density to prevent oxide growth, however, the thick film regions
10 tend to interfere with the wire bonding process. An even distribution of BTA
will therefore maintain film density and minimize thickness across one entire
5 wafer surface.

15 Thus, successfully applying a passivation film depends upon a
combination of BTA concentration levels and the process parameters that affect
20 uniformity of the BTA coverage about the target BTA film thickness (less than or
equal to 20Å). Uniform BTA coverage is achieved mostly through ensuring
10 uniform coating of the solution comprising the BTA. Uniform solution coatings
25 are achieved through higher wafer and brush rotation speed. Also, the shape of
the brush affects uniformity. For example, flat brushes result in better global and
30 local solution uniformity as compared to brushes with nodules.

In one embodiment, a passivation application process implemented with:
15 a BTA concentration of 500ppm in DI water and a ph of 7.0; a solution flow rate
35 of 500 cc/min; a brush having nodule needles and a brush speed of 120 rpm; a
roller speed of 40 rpm; a wafer process time of 35 seconds; a brush force of 1.5 lbs
40 and a temperature of 25°C resulted in acceptably dense films that varied between
15-20Å in total thickness across the entire wafer. The minimum bound of the
20 passivation layer thickness is met since it is thick enough to prevent oxide
45 formation. Furthermore, the maximum bound is met since the film is thin
enough to enable the wire bonding.

5 In another embodiment, a passivation application process implemented
with: a BTA concentration of 100ppm in DI water and a ph of 7.0, a solution flow
10 rate of 500 cc/min; a flat brush at a speed of 139 rpm; a roller speed of 40 rpm; a
wafer process time of 35 seconds; a brush force of 1.5 lbs and a temperature of
5 25°C resulted in acceptably dense, 15Å films with little variation in thickness
15 across the entire wafer surface.

In both the embodiments above, insubstantial oxide growth (10-40Å)
20 occurred beneath the BTA layer during high temperature curing of the test
samples.

10 Finally, as discussed, the removal of the oxide and the application of the
25 passivation layer do not necessarily require a brush scrubbing apparatus. Nor
does the process require implementation immediately after the final CMP wafer
30 clean step. For example, the oxide layer may be removed by an immersion (e.g.,
bath) process or by a spray process.

15 Baths involve completely immersing the wafer in an oxide etchant
35 solution. Processing parameters include time, concentration, temperature and
the amount of agitation (if any) applied to the bath. The solution chemistry the
40 wafer is dipped into is generally the same as that used with the scrubber system.
The time may range from seconds to minutes depending on the concentration of
20 the solution and the amount of agitation supplied. Since oxide removal by bath
45 is fairly well known in the art, specific processing parameters may be readily
determined.

5 In another embodiment, the oxide may be removed by an acid spray.
Sprays involve spraying the wafer with an etchant solution. The processing
10 parameters associated with spraying include: volumetric flow rate of the
solution, linear flow rate of the solution, the spray angle, the acidic concentration
5 in the sprayed solution, the time and temperature. Again, since oxide removal
15 by spray is fairly well known in the art, specific processing parameters may be
readily determined.

20 The passivation layer may be applied by processes other than a brush
scrubbing as well. These include, among others: immersion (such as baths),
10 sprays and spin coats. Application of films by baths and sprays involve
25 substantially the same parameters discussed above. Spin coats involve time, spin
speed, flow rate and solution concentration. Again, since application of films by
30 these methods are well known in the art, specific processing parameters may
similarly be readily determined.

15 Finally, if process techniques other than a scrubbing system's are used
35 (and unless the process is performed in an oxygen free environment), the
passivation layer should be applied as quickly after the oxide is removed as
40 possible or practicable. Again, within 5 seconds is a good rule of thumb.
Furthermore, allowing the oxide etchant to remain on the wafer surface until the
20 passivation layer is applied should similarly expand the allowable time margin
45 between oxide removal and passivation layer application.

Claims

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CLAIMS

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What is claimed is:

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1 1. A method, comprising:

2 a) removing an oxide from a surface; and

3 b) commencing application of a passivation layer to the surface within 5

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4 seconds of the oxide removal.

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1 2. The method of claim 1 wherein the surface further comprises a copper

2 surface.

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1 3. The method of claim 2 wherein the copper surface further comprises a

2 bonding pad surface.

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1 4. The method of claim 1 wherein the removing an oxide further comprises

2 applying a solution comprising citric acid to the surface.

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1 5. The method of claim 1 wherein the removing an oxide further comprises

2 applying a solution comprising hydrochloric acid to the surface.

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- 1 6. The method of claim 1 wherein the application of a passivation layer further
2 comprises applying a solution comprising a member of the azole family.

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- 1 7. The method of claim 6 wherein the azole family member further comprises
2 BTA.

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- 1 8. The method of claim 1 wherein the passivation layer is completely applied
2 35 seconds after said commencing.

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- 1 9. A method, comprising:
2 applying a liquid to a brush;
3 applying to a semiconductor wafer surface the liquid with the brush; and
4 forming a layer on the semiconductor wafer surface by a chemical
5 reaction between the liquid and the semiconductor wafer surface.

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- 1 10. The method of claim 9 wherein the layer is 20Å or less.

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- 1 11. The method of claim 9 wherein the semiconductor wafer further comprises a
2 semiconductor wafer having metallization.

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- 1 12. The method of claim 9 wherein the semiconductor wafer surface further
2 comprises a bonding pad surface.

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1 13. The method of claim 9 wherein the brush is part of a wafer brush scrubbing
2 system.

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1 14. The method of claim 9 wherein the layer further comprises a passivation
2 layer.

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1 15. The method of claim 14 wherein the passivation layer further comprises a
2 member of the azole family.

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1 16. The method of claim 15 wherein the azole family member further comprises
2 BTA.

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1 17. A method, comprising:

2 a) removing a first layer from a wafer surface with a first liquid applied
3 with a first brush located in a brush system; and

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4 b) applying a second layer to the wafer surface with a second liquid
5 applied with a second brush located in the brush system, the second
6 liquid having a reaction with the wafer surface to form the second
7 layer.

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1 18. The method of claim 17 wherein the second layer is 20Å or less.

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1 19. The method of claim 17 wherein the first layer further comprises an oxide.

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1 20. The method of claim 19 wherein the first liquid is a solution.

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1 21. The method of claim 20 wherein the solution comprises citric acid.

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1 22. The method of claim 20 wherein the solution comprises hydrochloric acid.

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1 23. The method of claim 17 wherein the second layer further comprises a
2 passivation layer.

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1 24. The method of claim 23 wherein the passivation layer further comprises a
2 member of the azole family.

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1 25. The method of claim 24 wherein the azole family member further comprises
2 BTA.

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1 26. The method of claim 17 wherein the semiconductor wafer further comprises
2 a semiconductor wafer having metallization.

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1 27. The method of claim 26 wherein the semiconductor wafer further
2 comprises a bond pad.

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1 28. The method of claim 27 further comprising applying a bond to the bond
2 pad through the second layer.

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1 29. The method of claim 17 wherein said first brush and said second brush are
2 the same brush.

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1 30. An apparatus, comprising:
2 a supply line configured to apply a liquid to a brush; and
3 the brush located over the surface of a wafer, the brush used to form a layer
4 on the wafer surface with the liquid.

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1 31. The apparatus of claim 30 wherein the liquid further comprises a member
2 of the azole family.

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1 32. The apparatus of claim 31 wherein the liquid further comprises BTA.

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1 33. The apparatus of claim 30 wherein the brush is located within a scrubbing
2 station of a brush system.

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1 34. A method, comprising:

2 a. removing an oxide layer from a wafer surface with a first liquid applied

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3 with a first brush located in a brush system;

4 b. applying a passivation layer to the wafer surface with a second liquid

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5 applied with a second brush located in the brush system, the liquid

6 having a reaction with the wafer surface to form the second layer; and

7 c. applying a bond to the wafer surface by punching through the

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8 passivation layer.

1 35. The method of claim 34, wherein said wafer surface further comprises a

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2 copper bond pad.

1 36. The method of claim 34 wherein said second solution comprises a member

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2 of the azole family.

1 37. The method of claim 36 wherein said second solution further comprises

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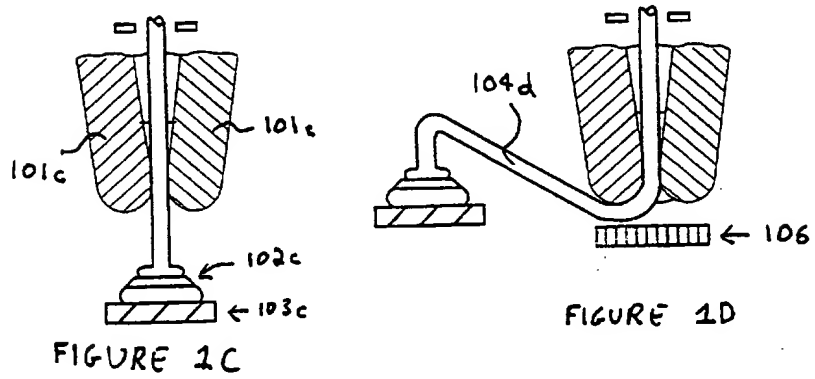
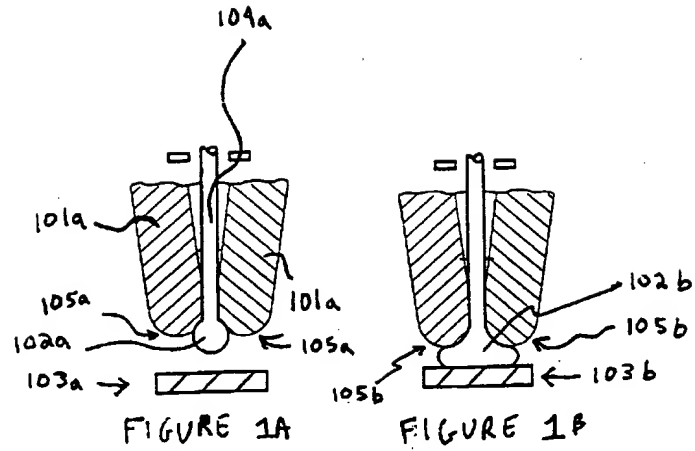
2 BTA.

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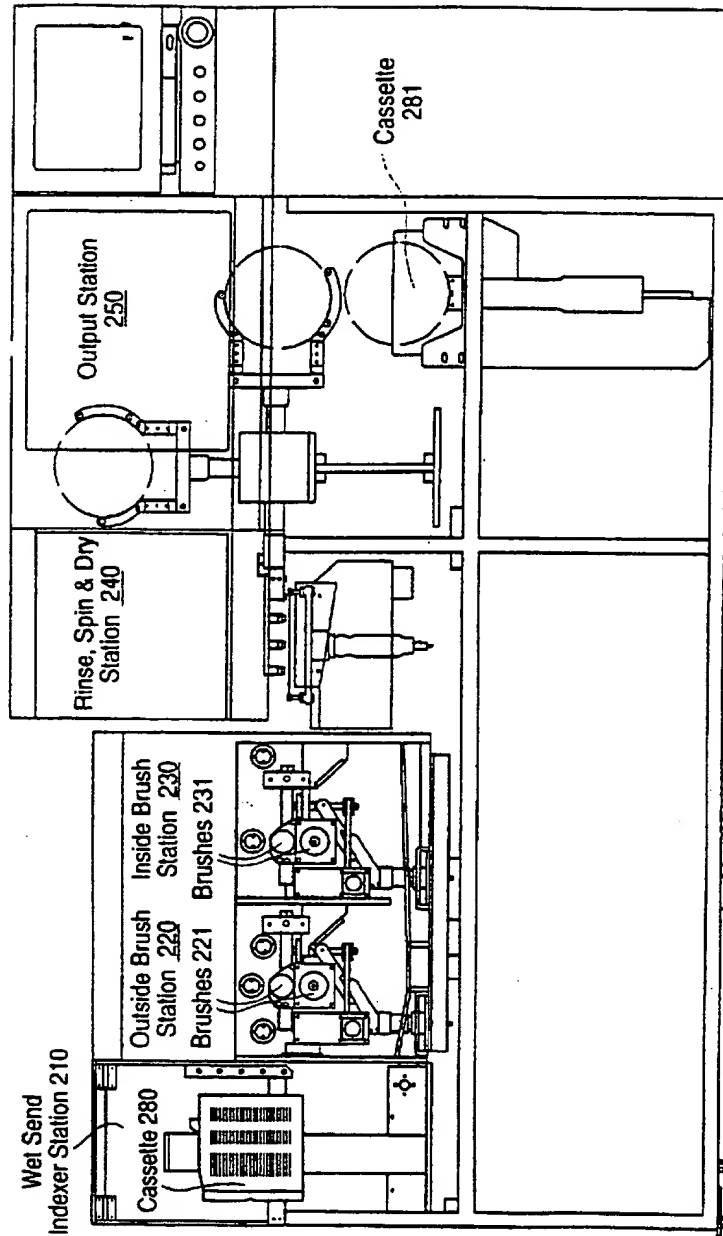


FIG. 2

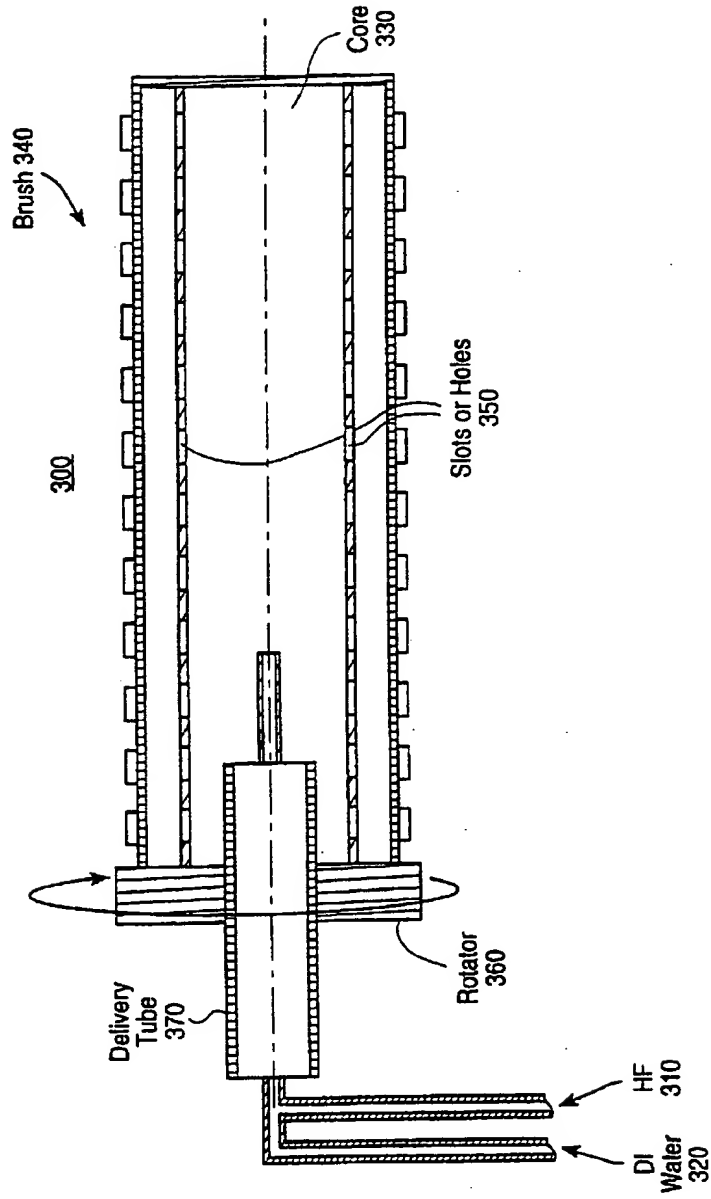


FIG. 3

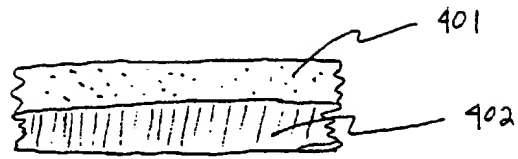


FIGURE 4A

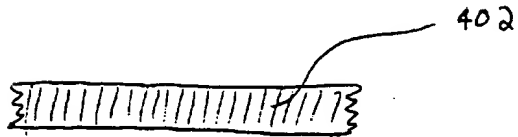


FIGURE 4B

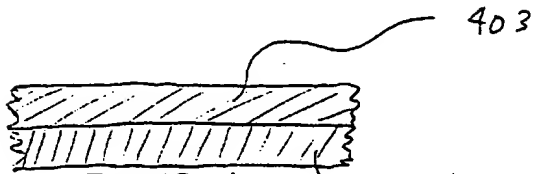


FIGURE 4C

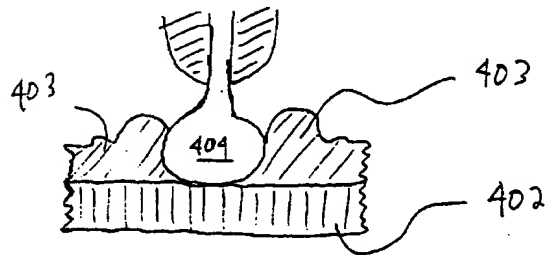


FIGURE 4D

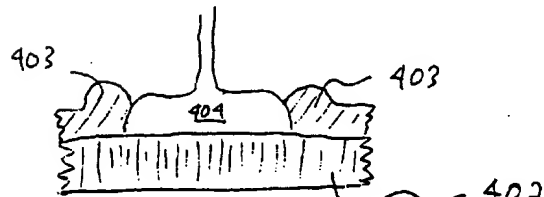


FIGURE 4E